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(54) **USE OF SYNTHETIC LUBRICATING OIL BASED ON POLYESTER AS LUBRICANT IN REFRIGERATORS**

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UTILISATION D'HUILE LUBRIFIANTE SYNTHETIQUE A BASE DE POLYESTER COMME LUBRIFIANTE POUR UN REFRIGERATEUR

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EP 0 452 509 B9

Description

The present invention relates to the use of a polyester synthetic lubricating oil and more particularly to a polyester synthetic lubricating oil suitable as a lubricating oil for a refrigerating machine. Still more particularly, it pertains to a polyester synthetic lubricating oil which has favorable miscibility with hydrogen-containing fluorocarbons (hydrogen-containing fluoroalkanes) (hereinafter referred to as "hydrogenated Flon compounds") such as 1,1,1,2-tetrafluoroethane (hereinafter referred to as "Flon 134a") capable of being used as replacements of fluorocarbons (Flon compounds) such as dichlorodifluoromethane (hereinafter referred to as "Flon 12") as refrigerants now causing a serious environmental pollution problem, and at the same time, is excellent in lubrication performance and particularly suitable as a lubricating oil for a compression-type refrigerating machine.

BACKGROUND ART

As a general rule, a lubricating oil, especially that for a refrigerator (refrigerating machine) is required to have favorable miscibility with an refrigerant used in a refrigerator. As an refrigerant for a compression-type refrigerator, Flon 12 or the like has heretofore been used. Flon 12, however, has recently been revealed as one of the causes of environmental pollution. As such, particular attention is being paid to hydrogenated Flon compounds such as Flon 134a as replacements.

As lubricating oils having favorable miscibility with the above Flon 134a, for example, Ulcon LB-165 and LB-525 (trade name, both produced by Union Carbide Co., Ltd.) composed of polyalkyleneglycol has been known, and it was reported that these lubricating oils are miscible with Flon 134a over the entire proportions at a low temperature of at least -50°C ("Research Disclosure", No. 17463 (October, 1978)). In addition, high viscosity refrigerator oil compositions employing polyoxypropylene glycol monobutyl ether as a base oil been known (Japanese Patent Publication No. 42119/1982).

Nevertheless, these lubricating oils are poly(alkylene glycol) derivatives, having polypropylene glycol with hydroxyl group at one terminal and an n-butyl ether bond at the other terminal, have comparatively good miscibility with Flon 134a at lower temperature, but do not have sufficient miscibility with Flon 134a at higher temperature, and for example, Ulcon LB-525 as described above is known to cause phase separation from Flon 134a at room temperature (Specification of US Pat. No. 4755316).

Aside from the above compounds polyglycol having at least two hydroxyl groups in a molecule is proposed as a substance having favorable miscibility with Flon 134a (Specification of US Pat. No. 4755316). However, the above disclosed polyglycol has not necessarily sufficient miscibility with Flon 134a.

On the other hand, Flon 134a and compounds capable of dissolving it were proposed for use in absorption-type refrigerators (Japanese Patent Application Laid-Open No. 79175/1981). The absorption-type refrigerators, however, differ widely in mechanism from the compression-type refrigerators as described above. Moreover, tetraethylene glycol dimethyl ether described in the Examples of the above Application is not suitable as a lubricating oil for compression-type refrigerators because of its particularly low viscosity.

GB-A-1 390 439 discloses a lubricant comprising a polyester being derived from polyhydric alcohols and dicarboxylic acids, especially sebacic acid, ethylene glycol, propylene glycol and 1,4-butanediol. Such lubricant is used in a 2-stroke engine, fed with a conventional fuel.

In GB-A-2 216 541 a working fluid/lubricant combination for use in a mechanical vapour recompression type heat transfer device wherein the working fluid comprises a hydrofluorocarbon, hydrochlorofluorocarbon or chlorofluorocarbon and the lubricant comprises an ester having a molecular weight greater than 250, especially an alkyl ester of an aliphatic or aromatic carboxylic acid.

EP-A 0 415 778 which has been published after the priority date of present invention discloses a refrigeration oil composition comprising (1) a hydrogenated fluoroethane and (2) an ester compound obtained from (2-a) an aliphatic polyhydric alcohol having 1 to 6 primary hydroxyl groups, (2-b) a saturated aliphatic monocarboxylic acid having 2 to 9 carbon atoms, straight or branched, or a derivative thereof and (2-c) a saturated aliphatic dicarboxylic acid having 2 to 10 carbon atoms, straight or branched, or a derivative thereof, said ester compound having a kinematic viscosity at 100°C of 1 to 100 cst.

As described hereinbefore, a lubricating oil for compression-type refrigerators having sufficiently good miscibility with Flon 134a as well as excellent lubrication performance has not been found yet, and its development has been eagerly desired.

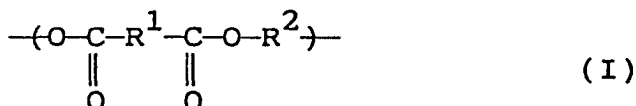
The present invention as disclosed hereunder has been accomplished in response to the above desire for the purpose of providing the use of a lubricating oil for compression-type refrigerators having excellent lubrication performance as well as favorable miscibility over the entire working temperature range with hydrogenated Flon compounds such as Flon 134a which can be substituted for refrigerant such as Flon 12 or other Flon compounds difficult to decompose, causing environmental pollution problems and at the same time, of providing a lubricating oil capable of

developing another use.

DISCLOSURE OF INVENTION

For the purpose as described above, the present inventors have made intensive research and development on an excellent lubricating oil. As a result, it has been found that a lubricating oil comprising as an essential component an aliphatic polyester derivative having a specific structure can meet the above purpose. The present invention has been accomplished on the basis of such a finding.

In more detail, the present invention provides as the first aspect thereof the use of a polyester synthetic lubricating oil which comprises, as an essential component, an aliphatic polyester derivative having a molecular weight in the range of 300 to 2000 and having at least one repeating unit represented by the general formula (I)



wherein R¹ is an alkylene group having 1 to 10 carbon atoms, and R² is an alkylene group having 2 to 10 carbon atoms or an oxaalkylene group having 4 to 20 carbon atoms.

Furthermore, the present invention provides as the second aspect thereof a method for lubrication characterized by lubricating a compression-type refrigerator wherein hydrogenated Flon compounds are used as a refrigerant by the use of the above-mentioned polyester synthetic lubricating oil. Still furthermore, the present invention provides as the third aspect thereof a compression-type refrigerator comprising a compressor, a refrigerant of hydrogenated Flon compounds, and the above polyester synthetic lubricating oil.

BEST MODE FOR CARRYING OUT THE INVENTION

As described hereinbefore, the lubricating oil used according to the present invention comprises, as an essential component, an aliphatic polyester derivative having at least one constitutional unit (repeating unit) represented by the general formula (I). In the formula, R¹ stands for an alkylene group having 1 to 10 carbon atoms. Specific examples are methylene group, ethylene group, propylene group, ethylmethylene group, 1,1-dimethylethylene group, 1,2-dimethylethylene group, n-butylethylene group, isobutylethylene group, 1-ethyl-2-methylethylene group, 1-ethyl-1-methylethylene group, trimethylene group, tetramethylene group, pentamethylene group and the like, and preferably an alkylene group having 6 or less carbon atoms. In the formula, R² designates an alkylene group having 2 to 10 carbon atoms or an oxaalkylene group having 4 to 20 carbon atoms. Specific examples of the alkylene group are same as those of the above-mentioned R¹ excluding methylene group, and preferably an alkylene group having 2 to 6 carbon atoms. Specific examples of oxaalkylene group include 3-oxa-1,5-pentylene group; 3,6-dioxo-1,8-octylene group; 3,6,9-trioxo-1,1,1-undecylene group; 3-oxa-1,4-dimethyl-1,5-pentylene group; 3,6-dioxo-1,4,7-trimethyl-1,8-octylene group; 3,6,9-trioxo-1,4,7,10-tetramethyl-1,11-undecylene group; 3-oxa-1,4-diethyl-1,5-pentylene group; 3,6-dioxo-1,4,7-triethyl-1,8-octylene group; 3,6,9-trioxo-1,4,7,10-tetraethyl-1,1,1-undecylene group; 3-oxa-1,1,4,4-tetramethyl-1,5-pentylene group; 3,6-dioxo-1,1,4,4,7,7-hexamethyl-1,8-octylene group; 3,6,9-trioxo-1,1,4,4,7,7,10,10-octamethyl-1,1,1-undecylene group; 3-oxa-1,2,4,5-tetramethyl-1,5-pentylene group; 3,6-dioxo-1,2,4,5,7,8-hexamethyl-1,8-octylene group; 3,6,9-trioxo-1,2,4,5,7,8,10,11-octamethyl-1,1,1-undecylene group; 3-oxa-1-methyl-1,5-pentylene group; 3-oxa-1-ethyl-1,5-pentylene group; 3-oxa-1,2-dimethyl-1,5-pentylene group; 3-oxa-1-methyl-4-ethyl-1,5-pentylene group; 4-oxa-2,2,6,6-tetramethyl-1,7-heptylene group; 4,8-dioxo-2,2,6,6,10,10-hexamethyl-1,11-undecylene group. R¹ and R² may be the same or different groups. In addition, R¹s or R²s in the above constitutional unit may be the same or different groups.

Furthermore, it is necessary for the aliphatic polyester derivative represented by the general formula (I) to have a molecular weight in the range of 300 to 2000 as measured by gel permeation chromatography (GPC). A molecular weight of less than 300 results in a too low kinematic viscosity, whereas that exceeding 2000 leads to the formation of waxy substance, both causing unsuitable lubricating oil.

The aliphatic polyester derivative as described above represented by the general formula (I) can be prepared by a variety of methods, for example, by the publicly known process for preparing polyester. Specific examples include (i) direct esterification process and (ii) ester exchange process as detailed hereunder.

(i) Direct esterification process

The direct esterification process is the process wherein a dihydric alcohol and a dibasic carboxylic acid are subjected to dehydration-condensation without any catalyst or in the presence of an acid catalyst. The reaction temperature during the process is usually in the range of 50 to 400°C, preferably 70 to 250°C and particularly preferably 100 to 180°C. If the reaction temperature is too high, decomposition or solidification takes place. On the other hand, if it is too low, the reaction hardly proceeds. The reaction time is usually in the range of one minute to 20 hours, preferably 10 minutes to 10 hours. The reaction may be carried out at ordinary pressure or a reduced pressure. Alternatively, two-stage reaction may be effected including half-ester synthesis at ordinary pressure followed by synthesis completion at a reduced pressure.

As the esterification catalysts, a cation-exchange resin, sulfuric acid, hydrochloric acid, p-toluene sulfonic acid, methanesulfonic acid, activated clay, zeolites of various types, silicotungstic acid, phosphotungstic acid, etc. may be usually used. The proportion in terms of molar ratio of a dihydric alcohol to a dibasic carboxylic acid each as raw material is usually in the range of 0.5 to 2.0, preferably 0.8 to 1.5 and particularly preferably 0.9 to 1.2.

The reaction process may be either batchwise or continuous.

(ii) Ester exchange process

The ester exchange process is the process wherein a dihydric alcohol and a diester of a dibasic carboxylic acid is subjected to condensation in the absence or presence of a catalyst. The reaction temperature during the process is usually in the range of 50 to 400°C, preferably 70 to 250°C and particularly preferably 100 to 180°C. If the temperature is too high, decomposition or solidification due to difficulty in polymerization control will occur. On the contrary, if it is too low, reaction rate is lowered. The reaction time is ordinarily in the range of one minute to 20 hours, preferably 10 minutes to 10 hours. The reaction may be carried out at ordinary pressure or a reduced pressure. Alternatively, two-stage reaction may be performed including half-ester synthesis at ordinary pressure followed by synthesis completion at a reduced pressure.

In the case of using a catalyst, an acid or base catalyst may be optionally selected. Also, a diester as raw material can be exemplified by a diester prepared by dehydration-condensation of a dibasic carboxylic acid and an arbitrary monohydric alcohol in addition to the above-mentioned dibasic carboxylic acid.

The proportion in terms of molar ratio of a dihydric alcohol to a diester of a dibasic carboxylic acid each as raw material is usually in the range of 0.5 to 2.0, preferably 0.8 to 1.5 and particularly preferably 0.9 to 1.2.

The reaction process may be either batchwise or continuous.

Examples of dibasic carboxylic acid to be used as raw material in the aforementioned (i) direct esterification process or (ii) Ester exchange process include, for instance, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, etc. Examples of diesters of dibasic carboxylic acid include dimethyl ester, diethyl ester each of the above dibasic carboxylic acid. As dihydric alcohols, ethylene glycol; propylene glycol; 1,2-butanediol; 1,3-butanediol; 2,3-butanediol; 1,4-butanediol; trimethylene glycol; neopentyl glycol (2,2-dimethylpropane-1,3-diol); pentamethylene glycol; hexamethylene glycol; heptamethylene glycol; nonamethylene glycol; decamethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; dipropylene glycol; tripropylene glycol; tetrapropylene glycol; dimer, trimer and tetramer each of 1,2-butylene oxide; dimer, trimer and tetramer each of 2,3-butylene oxide; 3-oxa-1-methylpentane-1,5-diol; 3-oxa-1-ethylpentane-1,5-diol; 3-oxa-1,2-dimethylpentane-1,5-diol; 3-oxa-1-methyl-4-ethylpentane-1,5-diol; 4-oxa-2,2,6,6-tetramethylheptane-1,7-diol; 4,8-dioxa-2,2,6,6,10,10-hexamethyl-1,11-undecane-1,11-diol, etc. are exemplified.

The above-mentioned process may be applied to the preparation of the aliphatic polyester derivatives to be used in the present invention. In addition to the above, modification may be made to improve miscibility, viscosity index and lubricity and to reduce hygroscopicity by allowing terminal hydroxyl groups in whole or in part to lead to the formation of ether. The hydrocarbon groups in the residual groups of the ether have preferably 1 to 10 carbon atoms.

In order to etherify the hydroxyl groups in the aforementioned aliphatic polyester derivative, there is normally used a process wherein a dialkyl sulfate having 1 to 10 carbon atoms, an alkyl halide or a sulfonic acid ester each having 1 to 10 carbon atoms is allowed to react with the above polyester derivative, or another process wherein the hydroxyl group in the aliphatic polyester derivatives is converted into a sulfonic acid ester or a halide, which thereafter is subjected to reaction with an aliphatic alcohol of 1 to 10 carbon atoms or alkali metal salt thereof.

In the lubricating oil used according to the present invention, for the purpose of maintaining the oil-film thickness necessary for lubrication, the kinematic viscosity of the lubricating oil before blending with a refrigerant is preferably in the range of 10 to 1000 mm²/s (10 to 1000 cSt). Accordingly, in the above processes, it is suggested that starting materials, other additives and reaction conditions for the aliphatic polyester derivative be selected so as to provide the lubricating oil with a kinematic viscosity within the aforementioned range.

In the lubricating oil used according to the present invention, single compound or a mixture of at least two com-

pounds from among the aliphatic polyester derivatives represented by the general formula (I) is employed, and as the case may be, together with other kind of lubricating oil. Further, various additives that are used in the conventional lubricating oils such as load resistant additives (extreme pressure agent, oiliness agent, anti-wear additive, etc.), chlorine capturing agent, antioxidants, metal deactivators, defoaming agents, detergent-dispersants, viscosity-index improvers, antirust agents, corrosion inhibitors, pour point depressants, etc. may be optionally blended according to demand or desire.

As the load resistant additives, there can be mentioned organic sulfide additives such as monosulfides, polysulfides, sulfoxides, sulfones, thiosulfates, sulfurized oil and fat, thiocarbonates, thiophenes, thiazoles, methanesulfonic acid esters, etc.; phosphate additives such as phosphoric monoesters, phosphoric diesters, phosphoric triesters (tricresyl phosphate) etc.; phosphite additives such as phosphorus monoesters, phosphorus diesters, phosphorus triesters, etc.; thiophosphate additives such as thiophosphoric acid triesters; fatty acid additives such as higher fatty acids, hydroxyaryl fatty acids, carboxylic acid-containing polyhydric alcohol esters, metallic soap, etc.; fatty acid ester additives such as polyhydric alcohol esters, acrylic esters, etc.; organic chlorine additives such as chlorinated hydrocarbons, chlorinated carboxylic acid derivatives, etc.; organic fluorine additive such as fluorinated aliphatic carboxylic acids, fluoroethylene resins, fluoroalkyl polysiloxanes, fluorinated graphite, etc.; alcohol additives such as higher alcohols, etc.; and metallic compound additives such as naphthenates (lead naphthenates), fatty acid salts (fatty acid lead), thiophosphates (zinc dialkyl dithiophosphate), thiocarbamates, organomolybdenum compounds, organic tin compounds, organogermanium compounds, boric acid esters, etc.

As the chlorine capturing agents, there can be mentioned compounds having glycidyl ether group, epoxy fatty acid monoesters, epoxidized fats and oils, compounds having epoxy cycloalkyl group, etc. As the antioxidants, there can be included phenols (2,6-di-tert-butyl-p-cresol), aromatic amines (α -naphthylamine), etc. As the metal deactivators, there can be mentioned benzotriazole derivatives, etc. As the defoaming agents, silicone oil (dimethylpolysiloxane), polymethacrylates, etc. can be included. As the detergent dispersants, sulfonates, phenates, succinimides, etc. can be included. As the viscosity index improvers, polymethacrylates, polyisobutylene, ethylene-propylene copolymer, hydrogenated styrene-diene copolymer, etc. can be exemplified.

In what follows, the present invention will be described in more detail by referring to Examples, which however, are not intended to limit the invention thereto.

Preparation Example 1

In a 1 liter three-necked glass flask equipped with a thermometer, a stirrer and a distillation head for distillate concentration, 165 g (1.03 mol) of diethyl malonate and 90 g (1.00 mol) of 2,3-butanediol were placed and heated in an oil bath at 160°C for 3 hours. After ethanol as the distillate was distilled away, reaction was carried out for 20 minutes under a reduced pressure (1.0 torr) to obtain 150 g of the objective poly(2,3-butylene malonate).

Preparation Example 2

The procedure of Preparation Example 1 was repeated except that the reaction was carried out for 15 minutes under a reduced pressure (1.0 torr) to obtain 153 g of the objective poly(2,3-butylene malonate).

Preparation Example 3

The procedure of Preparation Example 1 was repeated except that 165 g (1.03 mol) of diethyl malonate and 76 g (1.00 mol) of propylene glycol were used to obtain 145 g of poly(1,2-propylene malonate).

Preparation Example 4

The procedure of Preparation Example 1 was repeated except that 208 g (1.03 mol) of diethyl adipate and 76 g (1.00 mol) of propylene glycol were used to obtain 183 g of poly(1,2-propylene adipate).

Preparation Example 5

The procedure of Preparation Example 1 was repeated except that 208 g (1.03 mol) of diethyl adipate and 134 g (1.00 mol) of dipropylene glycol (product of Junsei Chemical Co., Ltd.) were used to obtain 207 g of diethyl adipate-dipropylene glycol polymer.

Preparation Example 6

The procedure of Preparation Example 1 was repeated except that 165 g (1.03 mol) of diethyl malonate, 38 g (0.50 mol) of propylene glycol and 45 g (0.05 mol) of 2,3-butanediol were used to obtain 128 g of diethyl malonate-propylene glycol-2,3-butanediol polymer.

Preparation Example 7

The procedure of Preparation Example 1 was repeated except that 179 g (1.03 mol) of dimethyl adipate and 104 g (1.00 mol) of neopentyl glycol were used to obtain 210 g of dimethyl adipate-neopentyl glycol polymer.

Preparation Example 8

The procedure of Preparation Example 7 was repeated except that the reaction was carried out for 18 minutes under a reduced pressure (1.0 torr) to obtain 215 g of dimethyl adipate-neopentyl glycol polymer.

Preparation Example 9

The procedure of Preparation Example 1 was repeated except that 179 g (1.03 mol) of dimethyl adipate and 134 g (1.00 mol) of dipropylene glycol were used to obtain 230 g of dimethyl adipate-dipropylene glycol polymer.

Preparation Example 10

The procedure of Preparation Example 9 was repeated except that the reaction was carried out for 15 minutes under a reduced pressure (1.0 torr) to obtain 234 g of dimethyl adipate-dipropylene glycol polymer.

Preparation Example 11

The procedure of Preparation Example 1 was repeated except that 406 g (1.03 mol) of di-3,5,5-trimethylhexyl adipate and 76 g (1.00 mol) of propylene glycol were used to obtain 180 g of di-3,5,5-trimethylhexyl adipate-propylene glycol polymer.

Preparation Example 12

The procedure of Preparation Example 11 was repeated except that the reaction was carried out for 15 minutes under a reduced pressure (1.0 torr) to obtain 187 g of di-3,5,5-trimethylhexyl adipate-propylene glycol polymer.

Preparation Example 13

The procedure of Preparation Example 1 was repeated except that 406 g (1.03 mol) of di-3,5,5-trimethylhexyl adipate and 134 g (1.00 mol) of dipropylene glycol were used to obtain 241 g of di-3,5,5-trimethylhexyl adipate-dipropylene glycol polymer.

Preparation Example 14

The procedure of Preparation Example 13 was repeated except that the reaction was carried out for 15 minutes under a reduced pressure (1.0 torr) to obtain 245 g of di-3,5,5-trimethylhexyl adipate-dipropylene glycol polymer.

Preparation Example 15

The procedure of Preparation Example 1 was repeated except that 406 g (1.03 mol) of di-3,5,5-trimethylhexyl adipate and 104 g (1.00 mol) of neopentyl glycol were used to obtain 212 g of di-3,5,5-trimethylhexyl adipate-neopentyl glycol polymer.

Preparation Example 16

The procedure of Preparation Example 15 was repeated except that the reaction was carried out for 15 minutes under a reduced pressure (1.0 torr) to obtain 218 g of di-3,5,5-trimethylhexyl adipate-neopentyl glycol polymer.

Examples 1 to 16 and Comparative Example 1

The measurements of the miscibilities with Flon 134a (1,1,1,2-tetrafluoroethane) were made for each of the samples, the polyesters obtained in the preceding Preparation Examples 1 to 16 and commercially available polyoxypropylene glycol mono-n-butyl ether by way of the following procedure:

A prescribed amount of a sample and Flon 134a were placed in a pressure glass ampule so that the sample would be 10% and 20% by weight, respectively to Flon 134a. The ampule was connected to a vacuum line and Flon 134a-gas line, subjected to vacuum degassing at room temperature and thereafter cooled with liquid nitrogen to take out the prescribed amount of Flon 134a containing the sample.

Subsequently, the ampule was sealed, heated in a thermostat to raise the temperature of the content from -40°C and the initial temperature of phase separation was measured. The higher the phase separation temperature is, the better the miscibility is. The results are shown in Tables 1 and 2.

Table 1

No.	Sample	Product origin (from)	kinematic viscosity at 40°C $10^{-2} \frac{m^2}{s}$ (cSt)	*1 Molecular weight	Initial temperature of phase separation (°C)
Example 1	poly(2,3-butylene malonate)	Prep. Example 1	144.3	544	>95
Example 2	poly(2,3-butylene malonate)	Prep. Example 2	85.1	487	>95
Example 3	poly(1,2-propylene malonate)	Prep. Example 3	85.8	455	70
Example 4	poly(1,2-propylene adipate)	Prep. Example 4	33.2	630	>95
Example 5	diethyl adipate-dipropylene glycol polymer	Prep. Example 5	18.5	431	>95
Example 6	diethyl malonate-propylene glycol-2,3 butanediol polymer	Prep. Example 6	125.2	571	>95
Comparative Example 1	polyoxypropylene glycol mono-n-butyl ether	UNILUBE-MB-14 ^{*2}	73.4	1200	38.5

*1 Weight average molecular weight as measured by GPC (gel permeation chromatography);
(standard reference material; polyethylene glycol)

*2 Brand name of product from Nippon Oils and Fats Co., Ltd.

Table 2

No.	Sample	Product origin (from)	Kinematic viscosity at 40°C $10^{-2} \text{ m}^2/\text{s}$ (cSt)	*1 Molecular weight	Initial temperature of phase separation (°C)
Example 7	dimethyl adipate-neopentyl glycol polymer	Prep. Example 7	274.2	650	70
Example 8	dimethyl adipate-neopentyl glycol polymer	Prep. Example 8	72.0	531	>95
Example 9	dimethyl adipate-dipropylene glycol polymer	Prep. Example 9	59.0	554	89
Example 10	dimethyl adipate-dipropylene glycol polymer	Prep. Example 10	37.4	483	>95
Example 11	di-3,5,5-trimethylhexyl adipate-propylene glycol polymer	Prep. Example 11	51.0	603	>95
Example 12	di-3,5,5-trimethylhexyl adipate-propylene glycol polymer	Prep. Example 12	30.0	531	>95
Example 13	di-3,5,5-trimethylhexyl adipate-dipropylene glycol polymer	Prep. Example 13	68.6	483	70
Example 14	di-3,5,5-trimethylhexyl adipate-dipropylene glycol polymer	Prep. Example 14	29.8	432	>95
Example 15	di-3,5,5-trimethylhexyl adipate-neopentyl glycol polymer	Prep. Example 15	73.0	578	78
Example 16	di-3,5,5-trimethylhexyl adipate-neopentyl glycol polymer	Prep. Example 16	33.2	454	>95

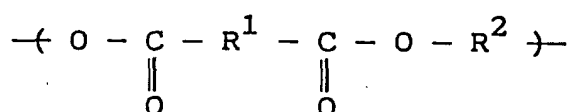
*1 Weight average molecular weight as measured by GPC (gel permeation chromatography);
(standard reference material; polyethylene glycol)

By virtue of surpassing miscibility with a refrigerant as well as excellent lubricating performance, the lubricating oil according to the present invention can be used for a variety of applications and is suitable for the lubrication of a refrigerator, especially of a compression-type refrigerator. Above all, different from the conventional lubricating oil, the lubricating oil according to the present invention has satisfactory miscibility with hydrogenated Flon compounds such as Flon 134a (most popular), 1,1-dichloro-2,2,2-trifluoroethane (Flon 123), 1-chloro-1,1-difluoroethane (Flon 142b), 1,1-difluoroethane (Flon 152a), chlorodifluoromethane (Flon 22), trifluoromethane (Flon 23), etc.

Accordingly, the lubricating oil according to the present invention is particularly well suited for a compression-type refrigerator in which a hydrogenated Flon compound, especially Flon 134a is used as a refrigerant.

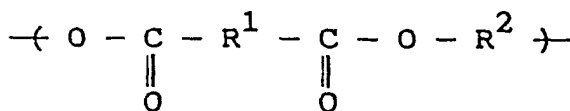
Claims

1. Use of a polyester synthetic lubricating oil which comprises, as an essential component, an aliphatic polyester derivative having a molecular weight in the range of 300 to 2000 and having at least one repeating unit represented by the general formula:



wherein R¹ is an alkylene group having 1 to 10 carbon atoms and R² is an alkylene group having 2 to 10 carbon atoms or an oxaalkylene group having 4 to 20 carbon atoms and wherein the terminal groups are hydroxy groups, carboxyl groups or esterified carboxy groups and has a kinematic viscosity at 40°C of 10 to 1000 mm²/s (10 to 1000 cSt), as a lubricant for compression type refrigerators in which hydrofluorocarbon is used as refrigerant.

2. The use according to Claim 1, wherein R¹ is an alkylene group having 1 to 6 carbon atoms and R² is an alkylene group having 2 to 6 carbon atoms.
3. The use according to Claim 1, wherein R¹ is an alkylene group having 1 to 6 carbon atoms and R² is an oxaalkylene group having 4 to 20 carbon atoms.
4. The use according to Claims 1 to 3, wherein said refrigerator is of compression type and uses 1,1,1,2-tetrafluoroethane as a refrigerant.
5. A compression-type refrigerator which comprises at least one compressor, a refrigerant consisting essentially of a hydrogen-containing fluorocarbon and said polyester synthetic lubricating oil which comprises, as an essential component, an aliphatic polyester derivative having a molecular weight in the range of 300 to 2000 and having at least one repeating unit represented by the general formula:

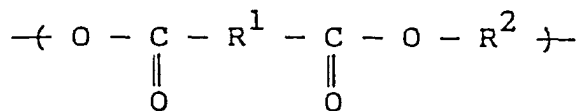


wherein R¹ is an alkylene group having 1 to 10 carbon atoms and R² is an alkylene group having 2 to 10 carbon atoms or an oxaalkylene group having 4 to 20 carbon atoms and wherein the terminal groups are hydroxy groups, carboxyl groups or esterified carboxy groups and has a kinematic viscosity at 40°C of 10 to 1000 cSt, as a lubricant for compression type refrigerators in which hydrofluorocarbon is used as refrigerant.

6. A compression-type refrigerator according to Claim 5, wherein said hydrogen-containing fluorocarbon to be used as a refrigerant is 1,1,1,2-tetrafluoroethane.

Patentansprüche

1. Verwendung eines synthetischen Polyesterschmieröls, das als wesentliche Komponente ein aliphatisches Polyesterderivat umfaßt, das ein Molekulargewicht im Bereich von 300 bis 2000 und wenigstens eine wiederkehrende Einheit hat, die durch die allgemeine Formel



repräsentiert wird, worin R¹ eine Alkylengruppe ist mit 1 bis 10 Kohlenstoffatomen, und R² ist eine Alkylengruppe mit 2 bis 10 Kohlenstoffatomen oder eine Oxaalkylengruppe mit 4 bis 20 Kohlenstoffatomen und worin die Endgruppen Hydroxygruppen, Carboxygruppen oder veresterte Carboxygruppen sind, und das eine kinematische Viskosität bei 40° C von 10 bis 1000 mm²/s (10 bis 1000 cSt) hat, als Schmiermittel für Kompressionskühlschränke, worin ein Fluorkohlenwasserstoff als Kältemittel verwendet wird.

2. Verwendung nach Anspruch 1, worin R¹ eine Alkylengruppe mit 1 bis 6 Kohlenstoffatomen und R² eine Alkylengruppe mit 2 bis 6 Kohlenstoffatomen ist.

3. Verwendung nach Anspruch 1, worin R¹ eine Alkylengruppe mit 1 bis 6 Kohlenstoffatomen und R² eine Oxaalkylengruppe mit 4 bis 20 Kohlenstoffatomen ist.

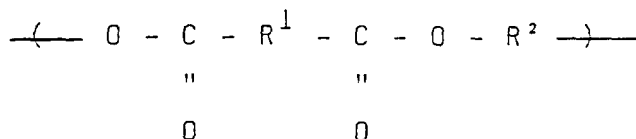
4. Verwendung nach Anspruch 1 bis 3, worin der Kühlschrank ein solcher vom Kompressionstyp ist und 1,1,1,2-Tetrafluorethan als Kältemittel verwendet wird.

5. Kompressionskühlschrank, der wenigstens aus einem Kompressor, einem aus im wesentlichen aus Wasserstoffenthaltenden Fluorcarbonen bestehenden Kältemittel und einem synthetischen Polyesterschmieröl besteht, das als wesentliche Komponente ein aliphatisches Polyesterderivat enthält, das ein Molekulargewicht im Bereich von 300 bis 2000 und wenigstens eine wiederkehrende Einheit hat, die durch die allgemeine Formel repräsentiert wird, worin R¹ eine Alkylengruppe ist mit 1 bis 10 Kohlenstoffatomen, und R² ist eine Alkylengruppe mit 2 bis 10 Kohlenstoffatomen oder eine Oxaalkylengruppe mit 4 bis 20 Kohlenstoffatomen und worin die Endgruppen Hydroxygruppen, Carboxygruppen oder veresterte Carboxygruppen sind, und das eine kinematische Viskosität bei 40° C von 10 bis 1000 mm²/s (10 bis 1000 cSt) hat, als Schmiermittel für Kompressionskühlschränke, worin ein Fluorkohlenwasserstoff als Kältemittel verwendet wird.

6. Kompressionskühlschrank nach Anspruch 5, worin das als Kältemittel verwendete wasserstoffhaltige Fluorcarbon 1,1,1,2-Tetrafluorethan ist.

Revendications

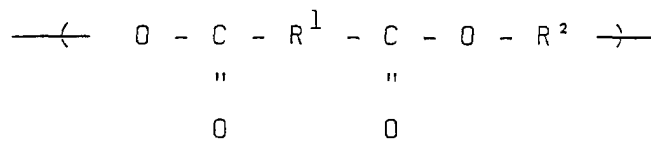
1. Utilisation d'une huile lubrifiante en polyester synthétique qui comprend, à titre d'un composant essentiel, un dérivé de polyester aliphatique ayant une masse moléculaire comprise entre 300 et 2000 et comportant au moins un motif récurrent de formule générale :



dans laquelle R¹ est un radical alkylène de 1 à 10 atomes de carbone et R² est un radical alkylène de 2 à 10 atomes de carbone ou un groupe oxaalkylène de 4 à 20 atomes de carbone et dans laquelle les groupes terminaux sont des groupes hydroxy, des groupes carboxyle ou des groupes carboxy estérifiés et ayant une viscosité cinématique à 40°C de 10 à 1000 mm²/s (10 à 1000 cSt), à titre de lubrifiant pour les réfrigérateurs du type à com-

pression dans lesquels un un hydrofluorocarbone est utilisé comme réfrigérant.

2. Utilisation selon la revendication 1, dans laquelle R¹ est un radical alkylène de 1 à 6 atomes de carbone et R² est un radical alkylène de 2 à 6 atomes de carbone.
3. Utilisation selon la revendication 1, dans laquelle R¹ est un radical alkylène de 1 à 6 atomes de carbone et R² est un groupe oxaalkylène de 4 à 20 atomes de carbone.
4. Utilisation selon les revendications 1 à 3, dans laquelle ledit réfrigérateur est du type à compression et utilise comme réfrigérant le 1,1,1,2-tetrafluoréthane.
5. Réfrigérateur du type à compression qui comprend au moins un compresseur, un réfrigérant consistant essentiellement en un fluorocarbonate contenant de l'hydrogène et ladite huile lubrifiante de polyester synthétique qui comprend, à titre d'un composant essentiel, un dérivé de polyester aliphatique ayant une masse moléculaire comprise entre 300 et 2000 et comportant au moins un motif récurrent de formule générale :



dans laquelle R¹ est un radical alkylène de 1 à 10 atomes de carbone et R² est un radical alkylène de 2 à 10 atomes de carbone ou un groupe oxaalkylène de 4 à 20 atomes de carbone et dans laquelle les groupes terminaux sont des groupes hydroxy, des groupes carboxyle ou des groupes carboxy estérifiés et ayant une viscosité cinématique à 40°C de 10 à 1000 mm²/s (10 à 1000 cSt), à titre de lubrifiant pour les réfrigérateurs du type à compression dans lesquels un hydrofluorocarbonate est utilisé comme réfrigérant.

6. Réfrigérateur du type à compression selon la revendication 5, dans lequel ledit fluorocarbonate contenant de l'hydrogène à utiliser comme réfrigérant est le 1,1,1,2-tétrafluoréthane.